



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B41M 3/14, G03C 1/73, 5/56	A1	(11) International Publication Number: WO 91/12139 (43) International Publication Date: 22 August 1991 (22.08.91)
(21) International Application Number: PCT/GB91/00195 (22) International Filing Date: 7 February 1991 (07.02.91) (30) Priority data: 9003014.9 9 February 1990 (09.02.90) GB (71) Applicant (for all designated States except US): COUR- TAULDS PLC [GB/GB]; 18 Hanover Square, London W1A 2BB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : SAMBROOK-SMITH, Colin, Peter [GB/GB]; 139 Black Prince Avenue, Coven- try CV3 5JH (GB). HAWKINS, Michael [GB/GB]; 147 Woodside Avenue South, Coventry CV3 6BJ (GB).		(74) Agent: HALE, Stephen, Geoffrey; J.Y. & G.W. Johnson, Furnival House, 14/18 High Holborn, London WC1V 6DE (GB). (81) Designated States: AT (European patent), AU, BE (Euro- pean patent), CA, CH (European patent), DE (Euro- pean patent), DK (European patent), ES (European pa- tent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (Euro- pean patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: IMAGING PROCESS (57) Abstract A process for imaging a film containing a reversible organic photochromic compound comprises exposing the film to UV light in one or more selected areas followed by treating it with a chemical reagent which reacts irreversibly with only the relatively colourless form of the photochromic compound. An alternative process comprises exposing the film to UV light and the chemical reagent followed by exposing it to high-frequency light in one or more selected areas to cause irreversible reaction. Preferably the photochromic compound contains a cyclic carboxylic acid anhydride ring and the reagent is ammonia or an amine. The imaged films are useful as security markings.		

IMAGING PROCESSTechnical Field

This invention relates to the formation of an image using a photochromic compound. The image formed can be used as an identifying mark, particularly a security marking, for goods, packages, documents or identification cards.

Background Art

A photochromic compound is a compound that undergoes a colour change when irradiated with light of a certain wavelength, which colour change may be reversible or irreversible. In general, the compounds are converted to a coloured form when irradiated with UV light and are converted to a pale or colourless form when irradiated with visible light. Such UV light and visible light may each be referred to as light which activates the photochromic compound. In some cases the coloured form may also be converted to the pale or colourless form under the action of heat. Examples of reversible photochromic compounds are spiropyrans and fulgides.

Photochromic compounds, particularly those which are colourless under white light, can be used for marking. The marking can be illuminated by UV light and an image previously invisible under white light can subsequently be seen. Unlike a fluorescent image, the image remains after exposure to UV has ceased, so that anyone observing the image need not be exposed to UV. A photochromic image can, for example, be printed on a substrate using an ink containing the photochromic compound.

European Patent Application 279600 describes a marking comprising a layer, preferably of film-forming material, which contains a photochromic compound. The photochromic compound is capable of changing colour when exposed to UV light, but it can be converted to a permanently non-photo-

chromic compound, preferably by over-exposure to UV light. An image is formed in the layer by converting the photochromic compound to a permanently non-photochromic compound in one or more selected areas. When the layer is
5 subsequently viewed under UV light a colourless image of non-photochromic compound can be seen on a background of coloured photochromic compound. Over-exposure in selected areas is preferably achieved by using a UV laser. Alternatively, over-exposure can be achieved by prolonged exposure
10 to light from a UV lamp through a mask.

It is an object of the present invention to provide an imaging process which is more rapid than the process of European Patent Application 279600 and which is not so dependent on the use of a UV laser.

15 U.S. Patent 3441411 describes a photographic method comprising exposing an imaging layer comprising an organic photochromic material to actinic electromagnetic radiation in image configuration of sufficient energy to convert at least a portion of said material from one photochromic
20 state to another, contacting said photochromic material with a reagent which is reactive with only one form of said photochromic material, and supplying sufficient heat energy to said photochromic material to cause a reaction between said reagent and one form of said photochromic material,
25 thereby forming a permanent differentially ascertainable reaction product in said layer. Although U.S. Patent 3441411 lists a wide variety of photochromic compounds, the only reagent which is described is an acid anhydride, which will react with photochromic compounds such as spiropyrans
30 which have phenol functionality in the coloured photochromic form. The chemically reacted material is visible as a yellow image.

The method of imaging disclosed in U.S. 3441411 has the disadvantage that the chemical reagent used to develop
35 the image remains in the article after imaging. The

undeveloped area of the image is therefore prone to undergo the development reaction whenever the article is exposed to electromagnetic radiation to reveal the image, so reducing the contrast between foreground and background. It is an object of the present invention to provide a means of avoiding such a disadvantage.

Disclosure of invention

According to a first aspect of the present invention, a process of imaging a film containing a reversible photochromic compound which can be converted by UV light from a relatively colourless form to a coloured form, in which process the film is exposed to UV light in one or more selected areas to convert the photochromic compound at least partially to its coloured form in the selected area or areas, the photochromic compound in the remaining area or areas being in the relatively colourless form, is characterised in that the film so exposed is treated with a chemical reagent which reacts with the relatively colourless form of the photochromic compound to form a relatively colourless substantially permanently non-photochromic compound or a precursor thereof but does not react with, or reacts reversibly with, the coloured form of the photochromic compound.

When the process is used for forming security markings, any reversible reaction product between the chemical reagent and the coloured form of the photochromic compound in the chemically treated film is allowed or caused to revert to the coloured form of the photochromic compound in the said selected area or areas. The film is then exposed to visible light to convert the coloured form of the photochromic compound into the relatively colourless form of the photochromic compound, thereby forming a relatively colourless film which has no apparent image but which has a latent image of relatively colourless photochromic compound against a background of relatively colourless substantially permanently non-photochromic compound, which image can be

seen after exposure to UV light.

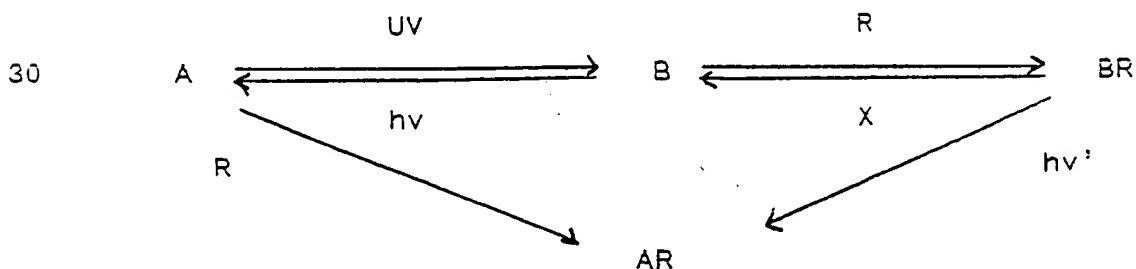
According to an alternative aspect of the present invention, a process of imaging a film containing a reversible photochromic compound which can be converted by UV
5 light from a relatively colourless form to a coloured form is characterised in that the film containing the photochromic compound in its coloured form is treated with a chemical reagent which reacts with the photochromic compound to form a temporarily non-photochromic compound,
10 which reaction is reversible for at least the coloured form of the photochromic compound, and the film is then exposed to high-frequency light in one or more selected areas, whereby the temporarily non-photochromic compound is converted to a relatively colourless substantially per-
15 manently non-photochromic compound in the selected area or areas but remains re-convertible into the photochromic compound in areas which are not exposed to the high-frequency light. By "high-frequency light" we mean light having a frequency within the visible or UV range and above
20 a minimum value depending on the particular photochromic compound and capable of effecting the said conversion.

To form a film suitable for security marking in this alternative aspect, after exposure of the film to high-frequency light the film is kept in conditions whereby the
25 temporarily non-photochromic compound is allowed or caused to revert to the coloured form of the photochromic compound in the non-exposed areas. The film is subsequently exposed to white light to convert the coloured form of the photochromic compound into the relatively colourless form of the
30 photochromic compound, thereby forming a relatively colourless film which has no apparent image but which has a latent image of relatively colourless substantially permanently non-photochromic compound against a background of relatively colourless photochromic compound, which image
35 can be seen after exposure to UV light.

It is an advantage of the present invention as compared with the procedure disclosed in US Patent 3441411 that the chemical reagent used to develop the image is removed from the article once the image has been developed in it, thus allowing repeated or extended examination of the developed latent image without reduction of contrast between foreground and background. It is a further advantage of the present invention that it is not required, as it is in the invention disclosed in US 3441411, that the chemical reagent used for development of the image react with only one of the forms of the photochromic compound.

The photochromic compound preferably contains a cyclic carboxylic acid anhydride group in both its coloured and its relatively colourless photochromic forms. One example of such compounds is provided by the fulgides. Another example is provided by the 3,4-diarylfuran-2,5-diones described in Japanese Published Unexamined Patent Application 88-24245. A further example is provided by the heliochromic compounds derived from fulgides described in British Patent Application 2146327. In such a case the chemical reagent with which the photochromic film is treated is preferably a reagent which will effect opening of the anhydride ring. Preferred examples of such reagents are ammonia and amines, especially primary or secondary amines.

The chemical and photochemical reactions involved in a preferred imaging process are summarised diagrammatically below:



where

A represents the photochromic compound in its relatively colourless form;

B represents the photochromic compound in its coloured form;

R represents the chemical reagent used to treat the film;

AR represents the reaction product of A with R;

BR represents the reaction product of B with R;

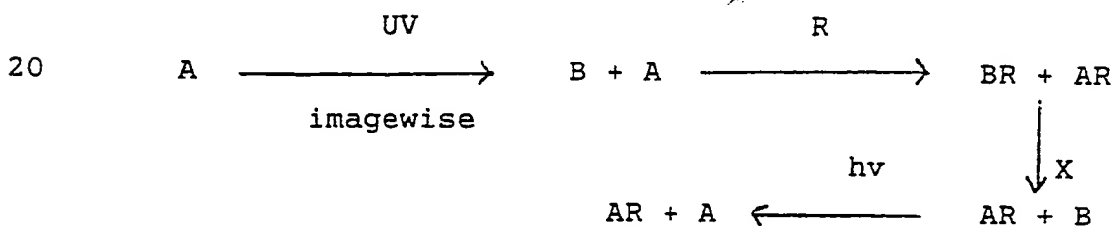
h ν represents visible light;

UV represents ultraviolet light;

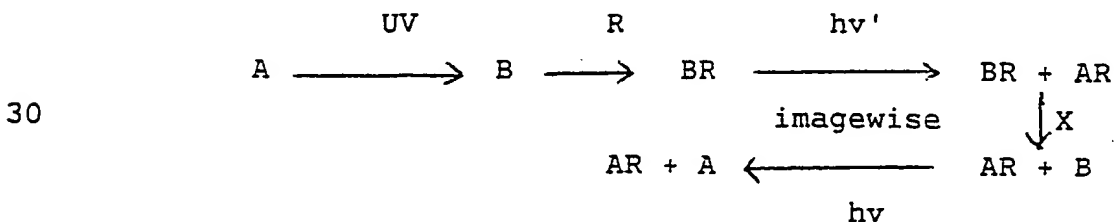
h ν' represents high-frequency light as hereinbefore defined; and

X represents a physical process, for example heating or evaporation, by which R is removed.

The first described process according to the invention, together with the subsequent steps necessary to produce a substantially colourless security-marked film, comprises the reaction scheme:

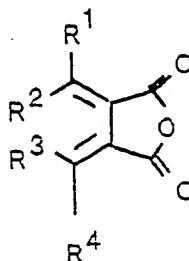


The alternative process according to the invention, together with the subsequent steps necessary to produce a substantially colourless security-marked film, comprises the reaction scheme:



The preferred photochromic compounds containing a cyclic carboxylic acid anhydride group are fulgides, as described for example in UK Patents 1442628 and 1464603, published UK Patent Application 2170202A and European
 5 Patent Application 279600 and in a paper by A. Kaneko et al in Bull. Chem. Soc. Japan 61, pages 3569-3573 (1988). The photochromic fulgides generally have the formula (in the relatively colourless form)

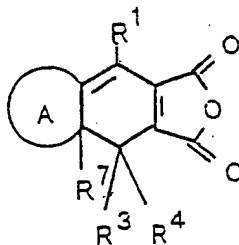
10



(I)

in which at least one of the substituents R^1 , R^2 , R^3 , and
 15 R^4 is an aromatic group (which term includes heterocyclic aromatic groups), the other substituents being hydrogen or monovalent hydrocarbon groups, for example C_1 - C_4 alkyl, particularly methyl, which can be substituted, provided that at least one of R^1 and R^2 and at least one of R^3 and
 20 R^4 is other than hydrogen. Preferably all the substituents are other than hydrogen. The fulgides derive their photochromic characteristics from their ability to undergo reversible ring closure. For example, where R^2 is the aromatic group, ring closure occurs between R^2 and the
 25 carbon atom to which R^3 and R^4 are attached. The fulgides in the coloured form thus generally have the formula:

30



(II)

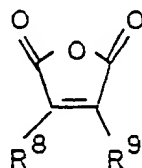
where A is a partially unsaturated ring derived from the

8

aromatic group R^2 and R^7 is hydrogen or a monovalent group present as a substituent in the aromatic group R^2 . Preferably R^7 is a group other than hydrogen, for example C_1-C_4 alkyl, particularly methyl.

- 5 Examples of preferred photochromic fulgides are those of formula (I) in which R^1 , R^3 and R^4 are all methyl and R^2 is a 2-alkyl-substituted 3-furyl or 3-thienyl or 3-pyrrolyl group, optionally having other substituents. Particularly preferred fulgides are those described in European Patent
 10 Application 279600 at page 4, lines 3 to 23 and the fulgides identified as 6, 7 and 9 in the above-mentioned paper by Kaneko et al.

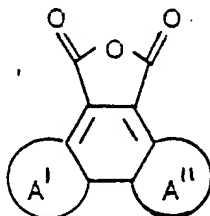
An alternative type of photochromic compound containing a cyclic carboxylic anhydride group is a 3,4-diaryl-
 15 furan-2,5-dione having the formula (in the relatively colourless form):



(III)

20

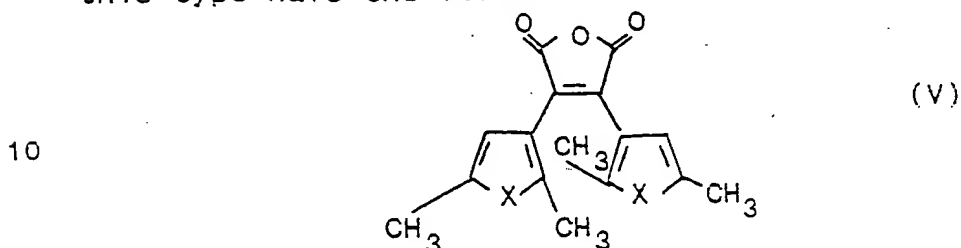
where R^8 and R^9 , which may be the same or different, are each aromatic groups and are preferably heterocyclic groups having an aromatic character, for example 3-furyl or 3-thienyl or 3-pyrrolyl groups, which may be substituted. This
 25 type of compound in the coloured form has the formula:



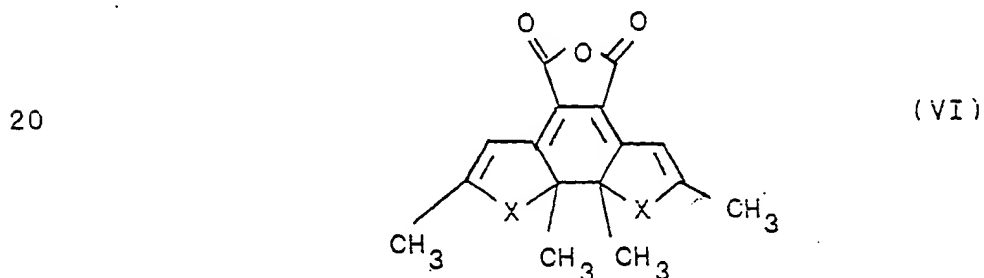
(IV)

where A' and A'' are partially unsaturated rings derived
 30 from R^8 and R^9 respectively. The groups R^8 and R^9 are

preferably each substituted by at least one alkyl, for example C_1-C_4 alkyl, particularly methyl, group, particularly in the ring-closing position (that is, the position adjacent to that at which the group R^8 or R^9 is attached to the anhydride ring). Examples of preferred compounds of this type have the formula:



where X represents an oxygen or sulphur atom or an NR^{10} group, where R^{10} represents a monovalent hydrocarbon group such as C_1-C_4 alkyl or phenyl. The thienyl compound (where X is sulphur) is particularly preferred. Such compounds in the coloured form have the formula:



The film used in the invention comprises a layer of film-forming material containing a photochromic compound, the film-forming material being substantially transparent to UV and visible light of the wavelengths that activate the photochromic compound. The photochromic compound is preferably incorporated in the film-forming material by dissolving or dispersing it in a solution of a film-forming polymer transparent to UV light of wavelength above 300nm. The most preferred film-forming polymer is cellulose acetate. Alternatives are other cellulose esters, polyesters, for example polyethylene terephthalate, acrylic polymers, for example polymethyl methacrylate, polyurethanes, olefin polymers, for example polyethylene or

SUBSTITUTE SHEET

polypropylene or ethylene-propylene copolymers or ethylene-vinyl acetate copolymers, vinyl polymers, for example polyvinyl acetate or polyvinyl chloride, polycarbonates and polyamides. The photochromic compound is preferably
5 dissolved in the solution so that it is essentially uniformly dispersed in the film formed. The photochromic fulgides for instance are soluble in a wide range of organic solvents, for example ketones such as acetone or methyl ethyl ketone, esters such as ethyl acetate, aromatic
10 hydrocarbons such as toluene, chlorinated hydrocarbons such as chloroform or methylene chloride, or ethers. They are not very soluble in water or aliphatic hydrocarbons and they may react to some extent with lower alcohols such as methanol and ethanol. The solution can be cast or coated
15 on a substrate to form a film. The photochromic fulgides can, for example, readily be incorporated in cellulose acetate film cast from acetone solution. The concentration of the photochromic compound is generally 0.03 to 10% by weight based on the film-forming material, preferably 0.1
20 to 5%, and most preferably 0.2 to 2%. The film is preferably colourless apart from the photochromic compound but alternatively can be lightly pigmented or dyed with a pigment or dye which is not degraded in UV or visible light.

25 When the film-forming material is a melt-extruded polymer, for example polyethylene, polypropylene, an ethylene-propylene copolymer or an ethylene-vinyl acetate copolymer, the photochromic compound can be dispersed in the polymer melt prior to extrusion, but care must be taken
30 not to cause thermal damage to the photochromic compound during extrusion. Useful photochromic compounds in this instance generally are those which are thermally stable to temperatures up to 100°C or even 180°C.

As an alternative method of incorporating the photo-
35 chromic compound, a film which is substantially transparent to UV and visible light at the wavelengths that activate

the photochromic compound may be 'dyed' with a solution of the photochromic compound. Any of the above-mentioned film-forming materials may be used to form the film, although this dyeing method is particularly suitable for materials into which the photochromic compound cannot be readily incorporated because, for example, it is insoluble in or reacts with the casting solvent or the extrusion temperature would damage the compound. Examples of such materials are certain polyesters and regenerated cellulose. This photochromic dyeing can be achieved by immersing the film in a dye bath containing the photochromic compound dissolved in a solvent which is a non-solvent for the film. The rate of dye uptake can, in general, be increased by increasing the temperature of the dye bath, especially by increasing it to a temperature above the glass transition point (but below the melting point) of the film. In addition, the rate may be increased by including in the dye bath a plasticiser which swells the film.

The chemical reagent used to effect ring opening of the cyclic carboxylic acid anhydride ring of the photochromic molecule is preferably ammonia or a primary or secondary amine, for example of the formula HNR^5R^6 , where R^5 is hydrogen, alkyl of 1 to 4 carbon atoms, hydroxyalkyl of 1 to 4 carbon atoms or aminoalkyl of 1 to 4 carbon atoms and R^6 is hydrogen, alkyl of 1 to 6 carbon atoms, hydroxyalkyl of 1 to 6 carbon atoms, aminoalkyl of 1 to 6 carbon atoms, aryl of 6 to 10 carbon atoms, aralkyl of 7 to 10 carbon atoms or a heterocyclic group. Ammonia is particularly preferred. Examples of amines which can be used are methylamine, ethylamine, isopropylamine, dimethylamine, diethylamine, ethylenediamine, ethanolamine, N-methylethanolamine and 2-(2-aminoethylamino)ethanol.

In the first process according to the invention the photochromic compound in its relatively colourless form is first exposed to UV light in one or more selected areas to

SUBSTITUTE SHEET

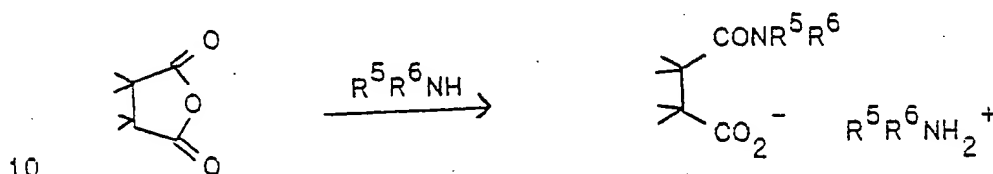
convert the photochromic compound at least partially to its coloured form in those areas. Colouration in selected areas can be achieved by exposure to a UV lamp through a mask, for example a 100 to 125 watt medium-pressure arc lamp. The characteristic colour of the photochromic compound is generally apparent in a second or two and typically reaches maximum intensity in 60 to 100 seconds. The time of UV exposure through the mask is most preferably 5 to 60 seconds. Alternatively, colouration in selected areas can be achieved by exposure to light from a UV laser. The use of a UV laser may be preferred if it is desired to mark security films with different images, for example serial numbers.

The film so exposed is then treated with a chemical reagent. The film is preferably immersed in a bath of the reagent, which may be a solution of the reagent or undiluted liquid reagent. For a gaseous reagent such as ammonia a chamber containing the gaseous reagent can alternatively be used. Any solvent used should preferably be inert to the photochromic compound and should not dissolve or substantially swell the film so that the film is intact and undistorted after the chemical treatment. Water is a preferred solvent for use with most film materials; for example ammonia and amines can be applied from aqueous solution. Water is a particularly good solvent for use with cellulose acetate film since cellulose acetate is permeable to water but is not dissolved or swollen by water. Aqueous ethanol is also a suitable solvent in many cases. Ammonia can for example be applied from the commercial solution sold as "0.880 ammonia" and containing about 35% by weight or from a more dilute solution, for example having a concentration of 10% or 20% by weight. Amines are preferably applied from solutions of concentration 10 to 70% by weight. Weaker solutions, for example containing 5% or even 1% by weight ammonia or amine, may also be used, generally at the expense of an increase in treatment time. The time of treatment is

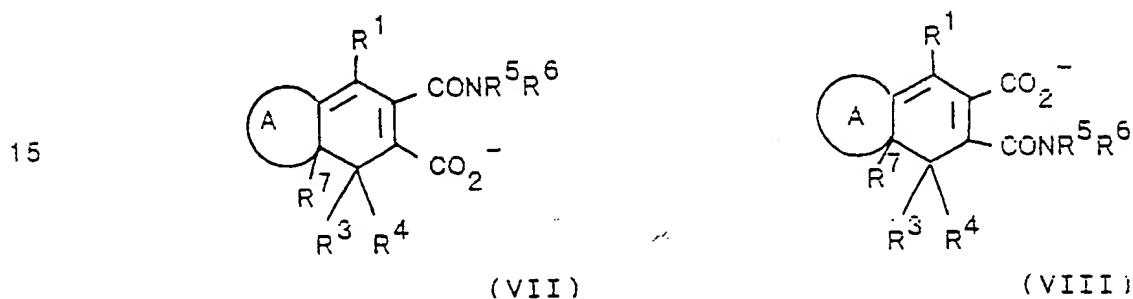
SUBSTITUTE SHEET

preferably in the range 1. second to 30 minutes; when treating a film containing a fulgide with an aqueous solution containing 10% or more by weight of ammonia or an amine times of 20 seconds to 20 minutes are generally used.

- 5 The reaction product of the photochromic compound containing an anhydride ring and ammonia or an amine is an amic acid or salt thereof:



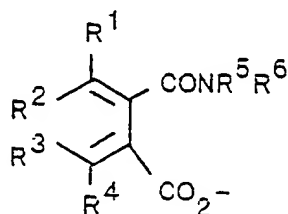
The coloured form of the fulgide (II) is believed to react with ammonia or an amine to form a mixture of the isomers:



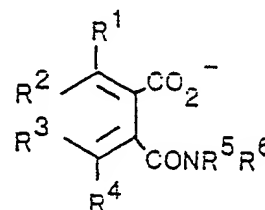
- 20 This product of reaction between the coloured form of a fulgide (II) and ammonia or an amine generally has a yellow colour. The reaction is reversible and the characteristic colour of the coloured form of the fulgide (II) will gradually reappear on standing, particularly under
- 25 conditions conducive to the removal of the ammonia or amine. It is a temporarily non-photochromic compound. Preferably the film is subjected to conditions under which the ammonia or amine is evaporated from the film. The film can for example be heated at a temperature which is below
- 30 the glass transition temperature of the film-forming material. The film can be heated by contact with a heated roller or in an oven. In general, more than 90%, for example 95%, of the colour of the photochromic compound

before chemical treatment is regained after 5 minutes at 80°C. If ammonia or a gaseous or highly volatile amine such as methylamine or ethylamine is used, application of heat to the film is not necessary, although it is generally preferred to apply heat to give a shorter treatment time. When ammonia is used heating times of for example 1 to 5 minutes can be used.

The relatively colourless form of the fulgide (I) is also believed to react with ammonia or amine to form a mixture of isomers:



(IX)



(X)

This product of reaction between the relatively colourless form of a fulgide (I) and ammonia or an amine is generally relatively colourless. Unlike the product of reaction derived from the coloured form of the fulgide (II), it will not undergo the reverse reaction to re-form the anhydride ring of the fulgide with any rapidity or to any significant extent. It is a relatively colourless substantially permanently non-photochromic compound. It may re-form the anhydride ring to some extent after a period of more than 3 months (that is, revert from AR to A within the sense of the first diagram above), but this is generally not significant in practical use as a security marking.

The chemically treated film is preferably kept in the dark during the process of reversion to the coloured form of the photochromic compound. It has been found that light of above a critical frequency (high-frequency light) may cause degradation of the reaction product to a relatively colourless permanently non-photochromic compound before reversion has taken place. It is believed that high-

frequency light causes ring opening of the amic acids (VII) and (VIII) to form the amic acids (IX) and (X), that is to say to form the same compounds as are present in the background areas of the film. The critical frequency is different for different photochromic compounds. The product derived from the reaction of the coloured form of 2-(1-(2,5-dimethyl-3-thienyl)ethylidene)-3-isopropylidene-succinic anhydride with ammonia, for example, will mainly revert to the coloured form of the fulgide on standing in daylight but will mainly be converted to amic acids (IX) and (X) under UV light or strong direct sunlight. The product derived from the reaction of the coloured form of 2-(1-(5-cyano-1,2-dimethyl-3-pyrryl)ethylidene)-3-isopropylidenesuccinic anhydride with ammonia will mainly be converted to amic acids (IX) and (X) even in indirect daylight.

The image of the coloured form of the photochromic compound in the selected areas against a background of relatively colourless substantially permanently non-photochromic compound can readily be used as a security marking by subjecting it to white light to convert the coloured form of the photochromic compound to the relatively colourless form. The image of the relatively colourless form of the photochromic compound is then substantially indistinguishable from the background of the relatively colourless substantially permanently non-photochromic compound. When the film is subsequently exposed to UV light, however, the photochromic compound is converted to its coloured form in the selected areas while the background remains relatively colourless; that is the image reappears.

The alternative process according to the present invention makes use of the phenomenon described above that high-frequency light will convert the amic acids (VII) and (VIII) corresponding to the coloured form of the photochromic compound to the relatively colourless substantially permanently non-photochromic amic acids (IX) and

SUBSTITUTE SHEET

(X). The minimum frequency of the high-frequency light will vary for different photochromic compounds. In general, UV light, for example light from a mercury arc lamp, will be of sufficiently high frequency for use with any photochromic fulgide. For certain fulgides, for example 2-(1-(5-cyano-1,2-dimethyl-3-pyrryl)ethylidene)-3-isopropylidenesuccinic anhydride, white light, for example from a daylight lamp, will be of sufficiently high frequency.

10 In this alternative process the photochromic compound is incorporated into a film as described above. The film is subjected to UV light, for example by exposure to a mercury arc lamp for 5 to 100 seconds, to convert the photochromic compound to its coloured form. The film is
15 then treated with the chemical reagent, for example ammonia or an amine. It is believed that a photochromic fulgide is thereby converted to amic acids (VII) and (VIII) over the whole area of the film. The film generally appears uniformly yellow. The film is then subjected to
20 high-frequency light, for example UV light, through a mask to form an image in one or more selected areas. Alternatively, the film can be imaged by a UV laser. It has been found that, when the fulgide 2-(1-(2,5-dimethyl-3-thienyl)ethylidene)-3-isopropylidenesuccinic anhydride is
25 used, treatment with ammonia according to this alternative process reduces the energy flux required from a UV laser to form the image by more than a hundredfold, compared with the process described in European Patent Application 279600. Although a laser is not required to achieve a short
30 exposure time, it may be preferred if security films are to be marked with different images, for example serial numbers. In the selected areas the photochromic compound is converted to a relatively colourless permanently non-photochromic compound. It is believed that the amic acids
35 (VII) and (VIII) are converted to amic acids (IX) and (X). The film thus has an image of the relatively colourless substantially permanently non-photochromic compound in the

selected areas against a background of the temporarily non-photochromic compound, for example the amic acids (VII) and (VIII). The image can generally be seen at this stage although not very distinctly, as a colourless image against a yellow background.

To form a film suitable for security marking from the film which has been exposed to high-frequency light in selected areas, the film is kept in conditions whereby the temporarily non-photochromic compound is allowed to revert to the coloured form of the photochromic compound in areas other than the exposed selected areas. Thus, it is believed that amic acids (VII) and (VIII) revert to fulgide (II). The preferred conditions are those conducive to the removal of the ammonia or amine used as chemical reagent. The film is preferably kept in the dark and is preferably heated at a temperature below the glass transition temperature of the film-forming material as in the first process according to the invention.

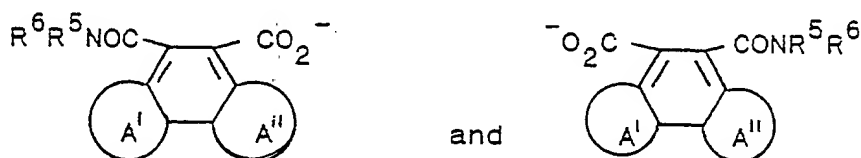
In the alternative process the imaging and heating steps can be combined if desired. In such a combined process the chemically treated film is covered with an opaque mask. The masked film is exposed to a floodlight which emits heat as well as light. For most photochromic compounds a UV floodlight is required, although for certain compounds such as cyano- or amido-substituted pyrryl fulgides a white light floodlight can be used. In the exposed areas the temporarily non-photochromic compound is converted to a substantially permanently non-photochromic compound. In the masked areas the heat and light emitted by the floodlight are absorbed by the opaque mask and transmitted as heat to the film, so that in the areas of the film beneath the mask the temporarily non-photochromic compound is converted by heat into the coloured form of the photochromic compound.

When the coloured form of the photochromic compound

SUBSTITUTE SHEET

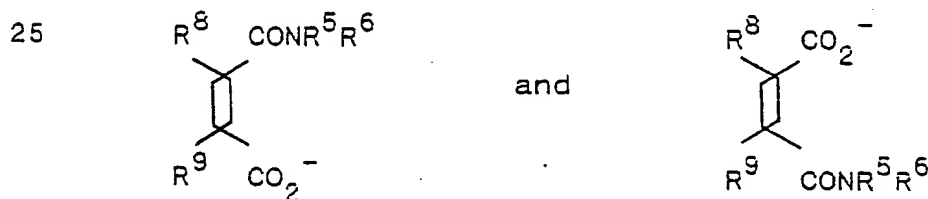
has reappeared the film is subsequently exposed to white light to convert the coloured form of the photochromic compound into the relatively colourless form of the photochromic compound. In the resulting film the selected areas of the film contain a relatively colourless substantially permanently non-photochromic compound while the background areas of the film contain the photochromic compound in its relatively colourless form. The film thus appears as a relatively colourless film with no apparent image. It has a latent image which can be seen after exposure to UV light as a colourless image against a background of the coloured form of the photochromic compound.

It is believed that the coloured form of a photochromic 3,4-diarylfuran-2,5-dione (IV) reacts with ammonia or an amine of the formula HNR^5R^6 to form the amic acids:



(XI)

which may be the same compound or isomers depending on whether R^8 and R^9 in (III) and (IV) are the same or different. This reaction is reversible on heating or on standing in the dark. It is believed that the relatively colourless form of the 3,4-diarylfuran-2,5-dione (III) reacts to form the amic acids:

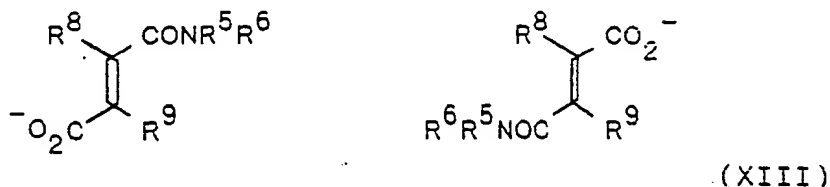


(XII)

The amic acid reaction product (XII) may revert to reform the anhydride ring to a significant extent on standing or heating, so that it is not substantially permanently

SUBSTITUTE SHEET

non-photochromic, unlike the amic acid reaction product (IX) and (X) derived from a fulgide. It can, however, undergo cis-trans isomerisation when irradiated by UV light, particularly by hard UV of wavelength 250 nm or less. The isomerisation product:



is a substantially permanently non-photochromic compound.

10 The amic acid reaction product (XII) can therefore be regarded as a precursor of a substantially permanently non-photochromic compound. When a 3,4-diarylfuran-2,5-dione is used in the first process according to the invention, an extra step of UV irradiation is therefore required after

15 the chemical treatment with ammonia or an amine. This irradiation should take place soon after chemical treatment, and before any heating step has taken place, to minimise any reversion to the coloured form of the photochromic compound.

20 A 3,4-diarylfuran-2,5-dione can be used in the alternative process of the invention without the need for an additional process step, provided that the high-frequency light to which the film is exposed imagewise is of sufficiently high frequency not only to cause ring opening of

25 the amic acid reaction product (XI) to the amic acid (XII) corresponding to the relatively colourless form of the photochromic compound but also of sufficiently high frequency to isomerise the amic acid (XII) to the substantially non-photochromic compound (XIII).

30 A 3,4-diarylfuran-2,5-dione (III) can be used in a further imaging process according to the present invention. In this process, a film containing the photochromic com-

SUBSTITUTE SHEET

pound (III) in its relatively colourless form is treated with a chemical reagent such as ammonia or an amine. It is believed that this effects opening of the anhydride ring, forming amic acid reaction product (XII). The product of chemical reaction is then exposed to UV radiation, preferably hard UV radiation of wavelength 250 nm or below, in one or more selected areas. In the selected areas it is believed that the amic acid reaction product (XII) is isomerised to (XIII), which is a substantially permanently non-photochromic compound. The film is then subjected to conditions conducive to removal of the ammonia or amine. Preferably the film is heated to cause evaporation of ammonia or amine from the film. In the background areas of the film which have not been exposed to UV radiation the anhydride ring will gradually re-form by reversion, so that the background areas of the film contain the relatively colourless form of the photochromic compound (III). The resulting film is useful as a security marking. It has no apparent image, but on subsequent irradiation with UV light the background areas will be converted to the coloured form (IV) of the photochromic compound. The exposed areas will be seen as a colourless image against a coloured background.

The invention is illustrated by the following Examples.

Example 1

2-(1-(2,5-dimethyl-3-thienyl)ethylidene)-3-isopropylidenesuccinic anhydride was incorporated in cellulose acetate film at a concentration of 1% by weight. A piece of the film was exposed to 5 minutes' UV irradiation from a Philips "Blacklight" fluorescent UV lamp array over the whole film. The film developed the magenta colour characteristic of this photochromic fulgide in its coloured form. The film was placed in 0.880 ammonia solution for 5 minutes, removed, washed with water and dried. The

appearance of the film was now light yellow. A mask (a zinc sheet with 3 mm diameter holes punched in it) was placed over the film which was then subjected to irradiation from the same UV lamps for 5 minutes. At the end of this period the lamps were switched off and the mask removed. The film was observed to exhibit an image of clear colourless circles on a yellow background. After 24 hours' storage in the dark the film was observed to exhibit an image of clear circles on a background of magenta. Bleaching the above film with white light for 10 seconds gave a colourless clear film useful as a security label. When the film was exposed to UV strip lamps, an image of clear slightly magenta-coloured circles on a strong magenta-coloured background appeared within seconds.

15

Example 2

A piece of cellulose acetate film containing 1% by weight 2-(1-(2,5-dimethyl-3-thienyl)ethylidene)-3-isopropylidenesuccinic anhydride was placed on a flat surface under the "Blacklight" UV lamp array. On top of the fulgide film was placed a mask of the type described in Example 1. The UV array was then switched on for 5 minutes to form a pattern of magenta circles. At the end of this period the UV strip lamps were switched off and the whole film submerged in a solution of 0.880 ammonia for 5 minutes. The film was removed from the solution, washed with water to remove excess ammonia solution and dried. The previously magenta areas were now coloured yellow. The remaining areas were clear and colourless. The sample was then stored in the dark at room temperature for 1 day. At the end of this period the yellow areas had recoloured to give a magenta colouration similar to that originally produced. The other areas remained clear and colourless. Bleaching of the film with white light for 10 seconds gave a film which was clear and colourless and useful as a security label. Exposure of the film to UV strip lamps produced an image of strongly coloured magenta circles with

SUBSTITUTE SHEET

a very pale magenta background within seconds.

Example 3

2-(1-(5-aminocarbonyl-1,5-dimethyl-3-pyrryl)ethyl-
idene)-3-isopropylidenesuccinic anhydride (XIV) was incor-
5 porated in cellulose acetate film at a concentration of
0.5% by weight. A piece of the film was placed on a flat
surface under a "Blacklight" lamp array and irradiated for
10 minutes. The resulting blue film was placed in a
solution of 0.880 ammonia for 5 minutes. At the end of
10 this period the film was washed in water and dried. The
appearance of the film was now yellow. The yellow film was
placed between a glass slide and a mask (a piece of zinc
sheet with 3 mm diameter holes punched in it). The slide,
film and mask were held together in close contact. The
15 masked sample was now held by hand in a beam of visible
light of wavelength above 420 nm for 30 seconds. At the
end of this period the film sample was removed from the
mask and glass slide. The film was observed to exhibit an
image of clear circles on a yellow background. After 24
20 hours' storage in the dark the film was observed to exhibit
an image of clear colourless circles on a blue background.
Bleaching of the film with white light for 10 seconds gave
colourless clear film free from any swelling. When the
film was subsequently exposed to UV light, an image of very
25 slightly blue circles on a strong blue background appeared
within seconds.

Example 4

Example 3 was repeated using a cellulose acetate film
containing 0.5% 2-(1-(5-cyano-1,2-dimethyl-3-pyrryl)ethyl-
30 idene)-3-isopropylidene succinic anhydride and 0.5% (XIV).
The film was treated in the manner described in Example 3.
Bleaching of the imaged film with white light gave a clear
colourless film. Subsequent exposure to UV light revealed
an image of very light blue circles on a blue background.

Examples 5 and 6

The photochromic cellulose acetate films of Examples 3 and 4 were treated as in Example 2, except that a 10 minute exposure to the UV lamps was used. This produced films when bleached with white light which were clear and colourless and free from swelling. Exposure of each film to UV strip lamps revealed an image of blue circles on a pale blue background.

Example 7

10 A piece of the film described in Example 4 10 cm square was exposed to 5 minutes' UV irradiation from a Philips "Blacklight" fluorescent UV lamp array. It was then placed in 0.880 ammonia solution for 5 minutes. The film was then removed and mounted on a card by means of
15 adhesive tape. The card was mounted on the drive shaft of an electric motor normal to the axis of rotation. The motor was turned on, so rotating the card at approximately 50 rpm. The card was then exposed to laser light of known power acting as a source of high-frequency light, incident
20 normally upon the card at a known distance from the axis of rotation, focussed to a known diameter, and for a set time. this procedure was repeated at different known distances from the axis of rotation to provide a series of concentric circles each exposed to a different known energy flux. The
25 film was then placed in an oven at 80°C for 30 minutes and exposed to daylight until the remaining coloured fulgide had been reconverted to the substantially colourless form, so providing a film containing a latent image of a substantially colourless permanently non-photochromic compound
30 against a background of substantially colourless photochromic compound. The film was then exposed to the UV lamp array as before to reveal the image. The diameter of the largest circle which showed no trace of the characteristic

SUBSTITUTE SHEET

colour of the fulgide to the eye was measured, and from this together with the known diameter of the laser beam and the known time of exposure the minimum energy flux required to produce total imaging was calculated. The image was, however, visible even in circles of large diameter.

Laser power was varied over the range 3.2 to 300 mW, beam diameter over the range 0.11 to 0.39 mm, and exposure time over the range 10 to 300 seconds.

Using a 488 nm laser line, it was calculated that an energy flux of 2.0 mJ/mm^2 was required to effect total imaging.

Example 8

Example 7 was repeated, except that the film described in Example 1 was used. Using 351 and 454 nm laser lines, it was calculated that energy fluxes of 3.9 mJ/mm^2 and 21 mJ/mm^2 respectively were required to effect total imaging.

Total imaging was also achieved using a 488 nm laser line at an energy flux of 680 mJ/mm^2 , but no lower energy flux was tested.

In a comparative experiment, the ammonia and oven treatments were omitted. Using a 351 nm laser line, it was calculated that an energy flux of 550 mJ/mm^2 was required to effect total imaging.

CLAIMS

1. A process of imaging a film containing a reversible photochromic compound which can be converted by UV light from a relatively colourless form to a coloured form, in which process the film is exposed to UV light in one or more selected areas to convert the photochromic compound at least partially to its coloured form in the selected area or areas, the photochromic compound in the remaining area or areas being in the relatively colourless form, characterised in that the film so exposed is treated with a chemical reagent which reacts with the relatively colourless form of the photochromic compound to form a relatively colourless substantially permanently non-photochromic compound or a precursor thereof but does not react with, or reacts reversibly with, the coloured form of the photochromic compound.

2. A process according to claim 1 for forming a film suitable for security marking, characterised in that any reversible reaction product between the chemical reagent and the coloured form of the photochromic compound in the chemically treated film is allowed or caused to revert to the coloured form of the photochromic compound in the said selected area or areas and the film is then exposed to visible light to convert the coloured form of the photochromic compound into the relatively colourless form, thereby forming a relatively colourless film which has no apparent image but which has a latent image of relatively colourless photochromic compound against a background of relatively colourless substantially permanently non-photochromic compound, which image can be seen after exposure to UV light.

3. A process according to claim 1, characterised in that the relatively colourless form of the photochromic compound reacts with the chemical reagent to form a precursor which can be converted by UV radiation to a relatively

SUBSTITUTE SHEET

colourless substantially permanently non-photochromic compound, and in that the film is UV irradiated after treatment with the chemical reagent, any reaction product formed between the coloured form of the photochromic compound and
5 the chemical reagent being substantially unaffected by the UV irradiation.

4. A process of imaging a film containing a reversible photochromic compound which can be converted by UV light from a relatively colourless form to a coloured form,
10 in which process the film is exposed to high-frequency light in one or more selected areas, characterised in that prior to the exposure to the high-frequency light the film containing the photochromic compound in its coloured form is treated with a chemical reagent which reacts with the
15 photochromic compound to form a temporarily non-photochromic compound which is converted to a relatively colourless substantially permanently non-photochromic compound in the selected area or areas during the said exposure to high-frequency light but which can be reconverted into the
20 photochromic compound in areas which are not so selected.

5. A process according to claim 4 for forming a film suitable for security marking, characterised in that after exposure of the film to high-frequency light the film is kept in conditions whereby the temporarily non-photochromic
25 compound is allowed or caused to revert to coloured form of the photochromic compound in areas other than the said selected area or areas and the film is subsequently exposed to white light to convert the coloured form of the photochromic compound into the relatively colourless form of the
30 photochromic compound, thereby forming a relatively colourless film which has no apparent image but which has a latent image of relatively colourless substantially permanently non-photochromic compound against a background of relatively colourless photochromic compound, which image
35 can be seen after exposure to UV light.

6. A process according to any of claims 1 to 5, characterised in that the film comprises a film-forming material substantially transparent to UV and visible light of the wavelengths that activate the reversible photo-
5 chromic compound.

7. A process according to claim 6, characterised in that the film-forming material is cellulose acetate.

8. A process according to claim 6 or 7, characterised in that a solution comprising the film-forming material,
10 the reversible photochromic compound and a solvent is cast to provide the film containing the reversible photochromic compound.

9. A process according to any preceding claim, characterised in that the reversible photochromic compound
15 comprises a cyclic carboxylic acid anhydride group.

10. A process according to claim 9, characterised in that the reversible photochromic compound is a fulgide.

11. A process according to claim 9, characterised in that the reversible photochromic compound is a 3,4-diaryl-
20 furan-2,5-dione.

12. A process according to any preceding claim, characterised in that the chemical reagent is ammonia or a primary or secondary amine.

13. A process according to any preceding claim,
25 characterised in that the chemical reagent is used in the form of an aqueous solution.

14. A process according to claim 12, characterised in that the chemical reagent is ammonia in the form of an aqueous solution containing 1 to 35% by weight ammonia.

SUBSTITUTE SHEET

15. A process according to claim 12, characterised in that the chemical reagent is an amine in the form of an aqueous solution containing 1 to 70% by weight amine.

16. A process according to any preceding claim,
5 characterised in that the film containing the reversible photochromic compound is treated with the chemical reagent for a time in the range 1 second to 30 minutes.

17. A process according to any preceding claim,
characterised in that the chemical reagent remaining in the
10 film after imaging or formed by reversion to the coloured form of the photochromic compound is removed from the film by evaporation.

18. A process according to any preceding claim,
characterised in that the source of UV light is a UV laser.

19. A process according to any of claims 1 to 17,
15 characterised in that the selected area or areas are defined by means of a mask.

20. A film containing a photochromic compound, which
is reversibly convertible between a coloured form and a
20 relatively colourless form and which in both forms has a cyclic carboxylic acid anhydride ring in its molecule,
characterised in that in one or more selected areas of the film the anhydride ring of the photochromic molecule has
been at least in part ring opened to an amic acid or salt
25 thereof.

21. A film according to claim 20, characterised in
that the photochromic compound is a fulgide.

22. A film according to claim 20 or 21, characterised
in that the amic acid or salt thereof has been produced by
30 reaction of the cyclic carboxylic acid anhydride ring with ammonia.

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/00195

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B41M3/14 ; G03C1/73 ; G03C5/56		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B41M ; G03C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,Y	US,A,3844792 (A.ZWEIG ET AL.) 29 October 1974 see column 3, line 51 - column 4, line 23 ---	1-22
Y	EP,A,279600 (COURTAULDS PLC) 24 August 1988 see page 5, line 40 - page 6, line 26 (cited in the application) ---	1-22
Y	US,A,3450533 (A.B.AMIDON ET AL.) 17 June 1969 see column 1, line 57 - column 2, line 63 see column 7, line 61 ---	1-22
Y	US,A,3450530 (A.B.AMIDON ET AL.) 17 June 1969 see column 1, line 57 - column 2, line 63 ---	1-22
Y	US,A,3441411 (A.B.AMIDON ET AL.) 29 April 1969 see column 5, lines 60 - 69 (cited in the application) ---	1-22
<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
29 MAY 1991	04. 07. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	BACON A.J. A.J. Bacon	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

SA 44987

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28/05/91

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3844792	29-10-74	None	
EP-A-279600	24-08-88	AU-B- 604093	06-12-90
		AU-A- 1246488	14-09-88
		EP-A- 0301057	01-02-89
		WO-A- 8806306	25-08-88
		JP-T- 1502303	10-08-89
		US-A- 4992347	12-02-91
		ZA-A- 8800796	04-08-88
US-A-3450533	17-06-69	None	
US-A-3450530	17-06-69	None	
US-A-3441411	29-04-69	GB-A- 1165215	24-09-69